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Mechanical, adhesive and thermodynamic properties of hollow nanoparticles

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Abstract

When sheets of layered material like C, WS₂ or BN are restricted to finite sizes, they generally form single- and multi-walled hollow nanoparticles in order to avoid dangling bonds. Using continuum approaches to model elastic deformation and van der Waals interactions of spherical nanoparticles, we predict the variation of mechanical stability, adhesive properties and phase behavior with radius R and thickness h . We find that mechanical stability is limited by forces in the nN range and pressures in the GPa range. Adhesion energies scale linearly with R , but depend only weakly on h . Deformation due to van der Waals adhesion occurs for single-walled particles for radii of few nm, but is quickly suppressed for increasing thickness. As R is increased, the gas-liquid coexistence disappears from the phase diagram for particle radii in the range of 1-3 nm (depending on wall thickness) since the interaction range decreases like $1/R$.

Introduction

The prototypical hollow nanoparticle is the buckyball C₆₀, which crystallizes into *fullerite*. Many other morphologies for carbon sheets have been found since the early 1990s, including fullerenes C_{*n*} of varying size, multi-walled fullerenes (*carbon onions*), and single- and multi-walled carbon nanotubes. Closed structures of carbon are formed in order to avoid dangling bonds at the edges of finite sized carbon sheets. This mechanism is generic for anisotropic layered material of finite size, and up to now more than 30 other materials have been prepared as hollow nanoparticles (see the reviews [1] and references therein). This includes the metal dichalcogenides MeX₂ (Me = W, Se, X = S, Se), BN, and GaN. Usually *inorganic fullerenes* like WS₂ and MoS₂ are multi-walled. In Fig. 1 we show transmission electron micrographs of MoS₂-particles which were synthesized by solid-gas reaction. Control of size and shape is rather difficult, as evidenced by the irregularly faceted shapes. However, the methods used for the synthesis of hollow nanoparticles are developing very rapidly, and it is to be expected that control of size, thickness and shape will become much better in the future.

Hollow nanoparticles combine covalent in-plane strength with flexible out-of-plane bending of thin films, which results in high mechanical stability. They interact by van der Waals (vdW) forces, which for example determine the material properties of fullerite [2] and the phase behavior of buckyballs [3]. VdW interactions become even more important for larger fullerenes, carbon onions and inorganic fullerenes; these materials, therefore,

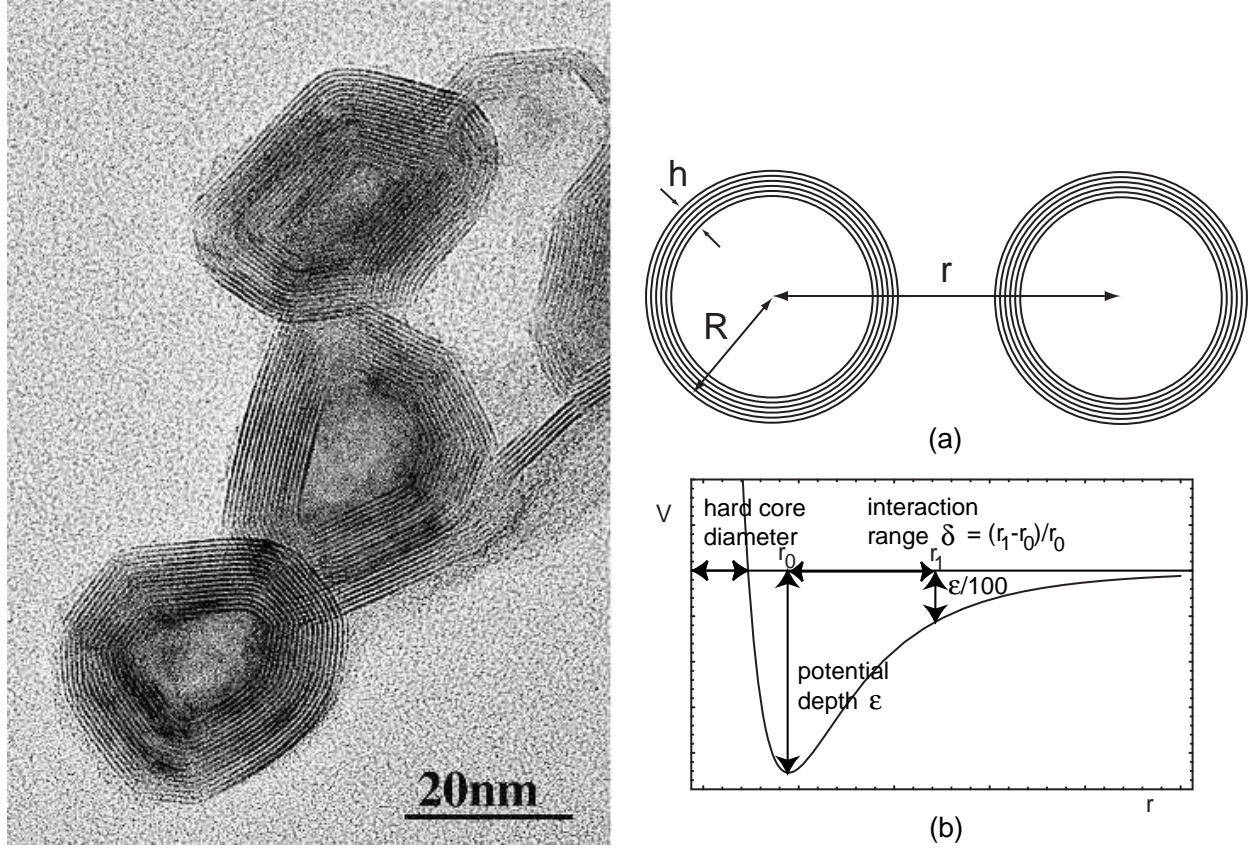


Figure 1: Left: Transmission electron micrographs of hollow MoS₂-nanoparticles (courtesy of R. Tenne). Van der Waals interactions leads to strong adhesion. The faceted shape is due to grain boundaries. Right: (a) Model for two spherical nanoparticles of radius R and thickness h each, interacting over a distance r . (b) The effective interaction potential V as a function of distance r is characterized by the hard core diameter $2R$, potential depth $\epsilon \sim R$ and interaction range $\delta \sim 1/R$.

feature a large degree of non-specific adhesion. In particular, vdW adhesion can lead to deformation of the hollow nanoparticles. For example, it has been found that carbon nanotubes adhering to each other or to flat surfaces show observable deformations for radii as small as 1 nm [4]. In the presence of local surface features like crystal steps, adhering nanoparticles will have spatially varying electronic properties due to spatially varying deformation.

Hollow nanoparticles may lead to new applications in nanoelectronics and -optics. In contrast to filled nanoparticles, they can also be used for storage and delivery systems. They show superior mechanical properties, like high flexibility, high tensile strength and light weight, which will lead to applications as ultra-strong fibers. Larger fibers can be produced using the cohesiveness provided by vdW interactions. Inorganic fullerenes have also been shown to offer favorable tribological properties [5]. Detailed investigations with the Surface Force Apparatus demonstrated that low friction and wear is caused by material transfer onto the sliding surfaces [6].

For these applications, a good theoretical understanding of the physical properties of hol-

low nanoparticles is important. Here we discuss structural properties of spherical hollow nanoparticles in a continuum approach that allows us to focus on unusual generic properties which result mainly from geometrical effects. In particular, we address mechanical properties, van der Waals interaction, thermodynamic behavior and deformation by adhesion. In this paper, we focus on the main results of our work; more details can be found elsewhere [7, 8].

Mechanical properties

During recent years, mechanical properties of fullerenes and carbon nanotubes have been extensively studied at the level of molecular calculations, that is by first principles, tight binding and force field techniques. The advantage of molecular models is that they can provide detailed quantitative predictions. For larger systems like multi-walled nanoparticles, their implementation becomes difficult due to computer time requirements. Here we use classical continuum elasticity theory, which is asymptotically correct for large systems and allows us to treat all these systems using the same framework. The large advantage of this approach is that it provides insight into the generic properties of these systems. Molecular calculations for carbon nanotubes have shown that the predictions of continuum elasticity theory persist well into the limit of radii smaller than 1 nm [9]. Recently this observation could be verified also for BN and MoS₂ nanotubes [10].

The layered material discussed here usually has a hexagonal lattice structure, for which elasticity theory [11] predicts that there are only two in-plane elastic constants and the sheet is elastically isotropic. Its deformation energy consists of stretching and bending terms. For single-walled carbon sheets, the in-plane stretching modulus $G \approx 3.6 \times 10^5$ erg/cm² and the out-of-plane bending rigidity $\kappa \approx 3 \times 10^{-12}$ erg. For both MoS₂ and WS₂, G is smaller by a factor 4 and κ is larger by a factor 5. For multi-walled nanoparticles, the elastic constants scale with thickness h as $G \sim C_{11}h$ and $\kappa \sim C_{11}h^3$, where C_{11} is the largest in-plane elastic constant of the corresponding layered material [12]. The values for C_{11} are 1060, 238 and 150×10^{10} erg/cm³ for C, MoS₂ and WS₂, respectively.

Stretching can be avoided completely by bending the sheet into a cylindrical nanotube. However, this is not possible for spherical nanoparticles, which we discuss here. The same holds true for saddle-like structures, and in general for all surfaces with non-zero Gaussian curvature. On a microscopic level, the requirement for non-zero Gaussian curvature also means that a flat sheet cannot be bent into a sphere without introducing defects. Continuum elasticity approaches to fullerenes therefore explicitly treated the 12 pentagonal defects necessary to close a sheet of carbon hexagons [13]. In order to avoid this complication, here we assume that the curvature generating defects are distributed in a homogeneous manner and result in a vanishing internal strain (like for a ping-pong ball). In this case, the hollow nanospheres can be modeled as elastic shells with thickness h and preferred radius R .

Mechanical collapse in tribological applications is likely to be caused by either direct forces or high pressure. In the latter case, an inward buckling instability occurs, since the pressure energy scales with a higher power of indentation H than the restoring elastic energy (H^2 versus $H^{3/2}$) [7]. Mechanical collapse is expected when indentation H becomes of the order of radius R . The critical pressure for collapse can then be estimated to be $p_c \sim G^{1/4}\kappa^{3/4}/R^{5/2}$. For buckyballs and typical inorganic fullerenes, this yields values

of 15 and 2 GPa, respectively. For nanoparticles, the corresponding forces are in the nN-range.

Van der Waals interaction and phase behavior

Since vdW interactions are very difficult to treat on a molecular level, a continuum approach is even more useful in this case. It is well known from colloid science that vdW interactions strongly depend on the geometry of the system under investigation. Geometrical aspects of vdW interactions are well treated in the Hamaker approach, in which an atomic Lennard-Jones interaction is summed in a pairwise manner over the relevant geometry and the molecular details of the interaction are lumped into the effective Lennard-Jones parameters σ and ϵ . For carbon, $\sigma = 3.5\text{\AA}$ and $\epsilon = 4.6 \times 10^{-15}$ erg [2]. The corresponding Hamaker constant A is in the order of 10^{-12} erg. For two buckyballs, the Hamaker approach for thin sheets leads to the *Girifalco potential* [2], which is considerably shorter ranged than a Lennard-Jones potential. Since a small range of attraction leads to the disappearance of the gas-liquid coexistence from the phase diagram [14], it has been suggested that buckyballs constitute the first non-colloidal system for which the gas-liquid critical point does not appear in the phase diagram. However, large scale simulations have shown that buckyballs indeed do show a gas-liquid coexistence, which extends roughly from 1900 to 2000°C [3].

For hollow nanoparticles in general, the effect of a finite thickness h becomes important. However, for nanoparticles in a crystal or adhering to a flat substrate or to each other, the distance of closest approach D between interacting particles is on an atomic scale. Under such conditions, the vdW interaction saturates on the atomic scale D with increasing thickness h . For example, the surface energy for the interaction with a halfspace scales as $\epsilon h/D^3$ and ϵ/D^2 for thin films and halfspaces, respectively, with the crossover occurring for $h = D$. Since $h \gtrsim D$ in our case, the surface energy is ϵ/D^2 independently of h and no significant scaling with thickness is expected.

For a more detailed investigation, one has to consider the general case of two nanospheres of finite thickness interacting in a pairwise manner by a Lennard-Jones potential [8]. The interaction energy can be written as $V = V_{R,R} + V_{R-h,R-h} - 2V_{R,R-h}$, where V_{R_1,R_2} is the interaction energy between two filled balls of radii R_1 and R_2 , respectively, which can be calculated analytically for a Lennard-Jones potential. In order to predict phase behavior, three quantities characterizing the resulting potential are especially important: the hard core diameter $2R$ sets the density scale, the potential depth sets the temperature scale, and the interaction range determines if a gas-liquid coexistence occurs (compare Fig. 1). Our full analysis has shown that for hollow nanoparticles of radius R and thickness h , the potential depth and interaction range scale linearly and inversely with R . Both quantities depend only weakly on h . In Fig. 2 we show our numerical results for the interaction range as a function of R and h . Recent work for the Double-Yukawa potential suggests that the gas-liquid coexistence disappears for an interaction range smaller than $\delta = 0.4$ [15]. Our analysis predicts that this happens for $R = 12\text{\AA}$ and $R = 35\text{\AA}$ for single- and multi-walled nanoparticles, respectively. For larger R , the critical point will disappear from the phase diagram.

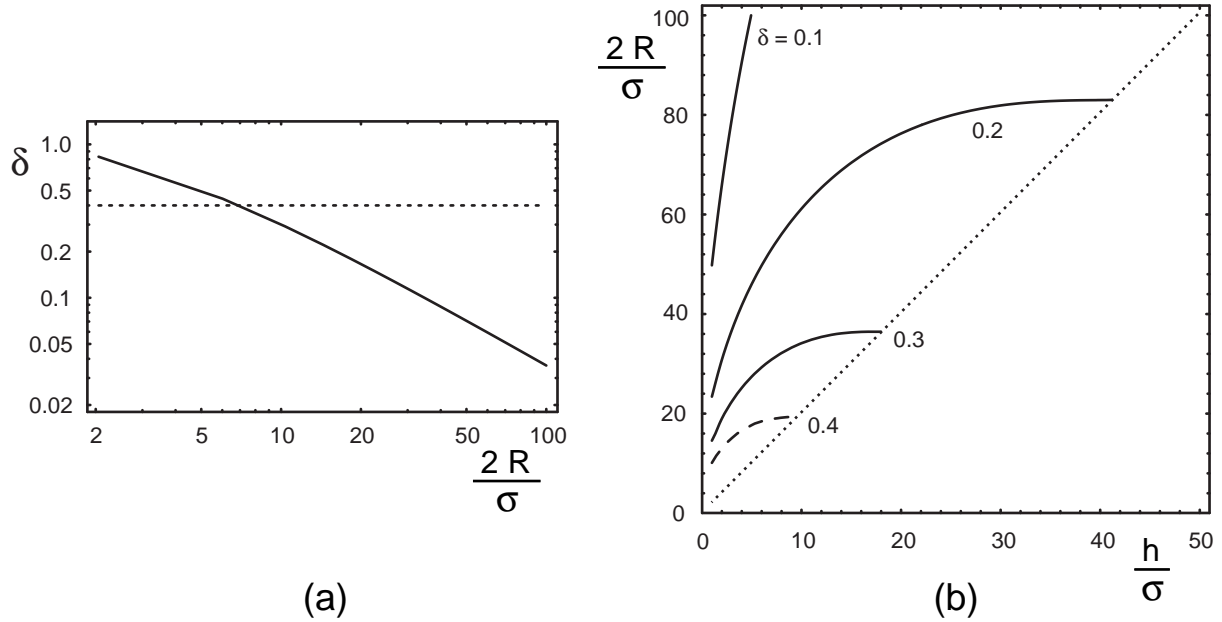


Figure 2: Numerical results for the interaction range δ (a) for single-walled nanoparticles as a function of radius R and (b) for multi-walled nanoparticles as a function of radius R and thickness h . $\sigma = 3.5 \text{ \AA}$ is the atomic length of the Lennard-Jones potential. The gas-liquid coexistence is expected to disappear from the phase diagram for $\delta < 0.4$ (dashed lines).

Deformation due to adhesion

We consider the case where a spherical hollow nanoparticle is indented a distance H due to adhesion to a flat substrate. The vdW energy gained on adhesion can be estimated to be $E_{vdW} \sim (A/D^2)DH$ where A is the Hamaker constant and D an atomic cutoff [16]. The energy of deformation can be estimated to be $E_{el} \sim G^{1/2}\kappa^{1/2}H^2/R$. With increasing R , deformation becomes more likely, since both the vdW energy and deformability increase. However, deformability decreases rapidly with increasing thickness h , since $G^{1/2}\kappa^{1/2} \sim h^2$. Solving for the indentation H and using the values given above, it is found that for hollow carbon nanoparticles with few walls, H can be in the nm-range [7]. However, for typical inorganic fullerenes deformations are suppressed by the larger shell thickness h .

Finally we briefly discuss a nanotube adhering to a flat substrate. As explained above, nanotubes can be bent without being stretched. On deformation, one has to pay a bending energy per length of $E_{el}/L \sim \kappa H^2/R^3$. The gain in vdW energy scales as $E_{vdW}/L \sim AH/D^{3/2}R^{1/2}$. It follows that for carbon nanotubes with small thickness h , the indentation H can be in the nm-range for even smaller values of radius R than for hollow carbon nanoparticles.

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- [16] This estimate is valid for weak adhesion. In [7], we used an estimate for strong adhesion, $E_{vdW} \sim (A/D^2)RH$. Then the predicted deformation is larger by a factor of R/D , yet the general conclusions are the same.